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(54) **DEVICE FOR AND METHOD OF GENERATING OZONE**

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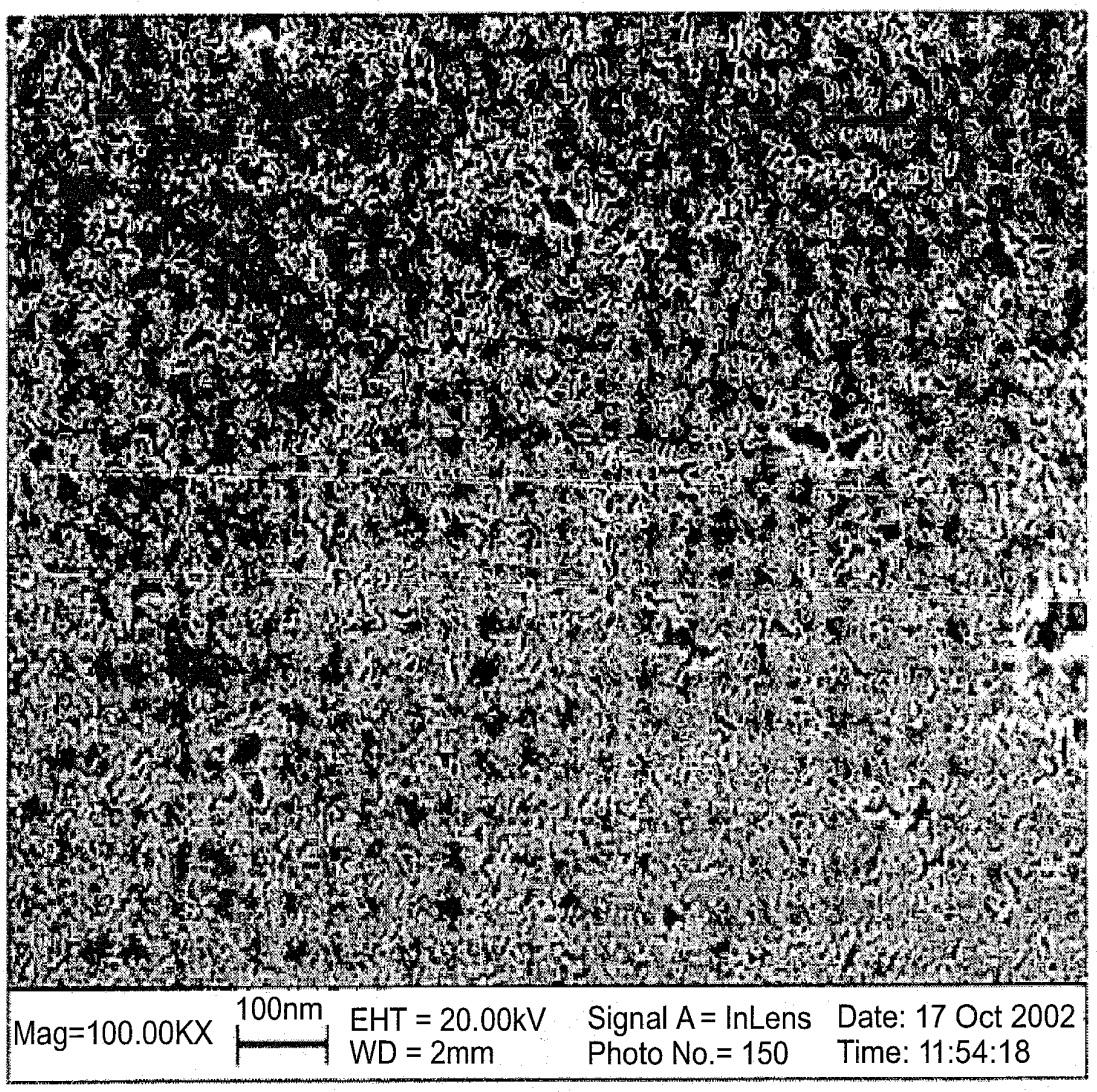
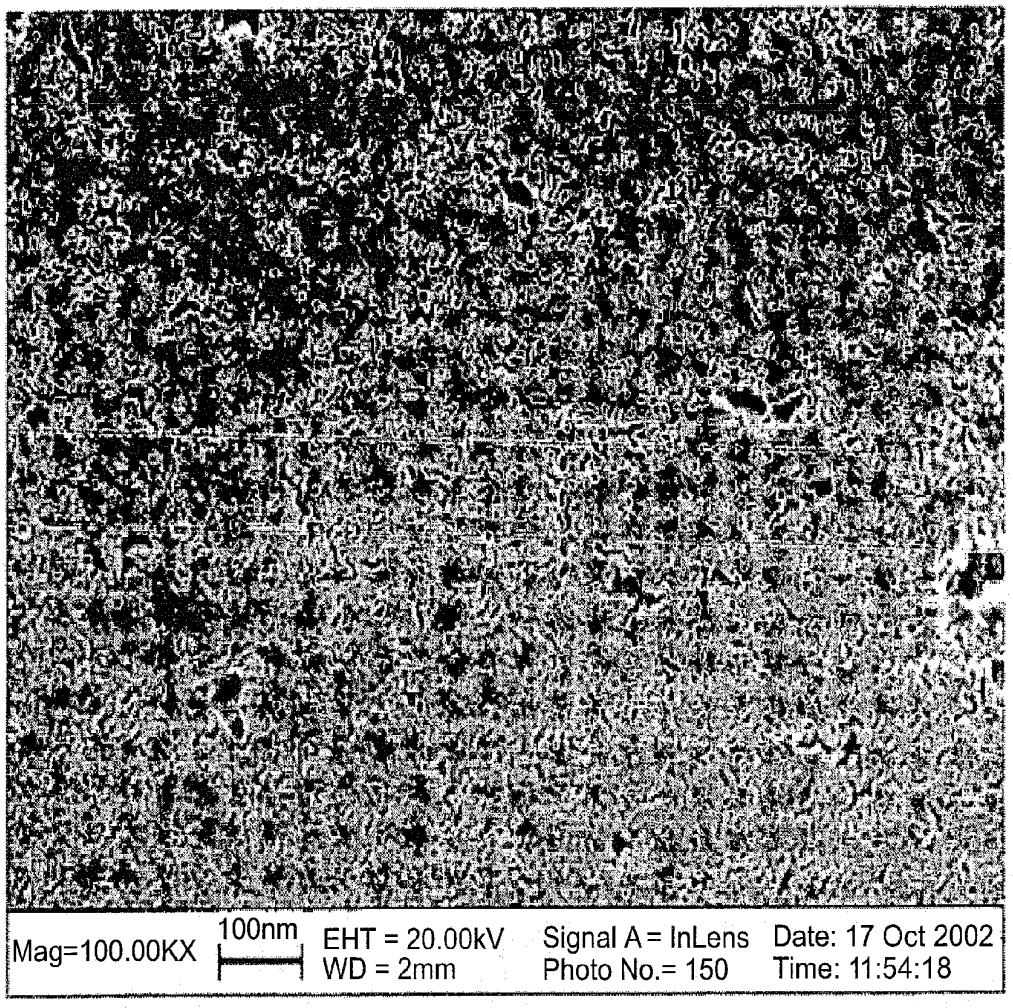
(57) **ABSTRACT**

The present invention can provide an electrode member having a substrate member and a coating member. The substrate member can be made of a material selected from the group consisting of titanium, gold coated titanium and other inert conducting materials. The coating member can have a tin dioxide modified by antimony. The electrode member of the present invention can be used for direct generation of ozone in water or through water into a gaseous state.




Mag=100.00KX
100nm
EHT = 20.00kV
WD = 2mm
Signal A = InLens
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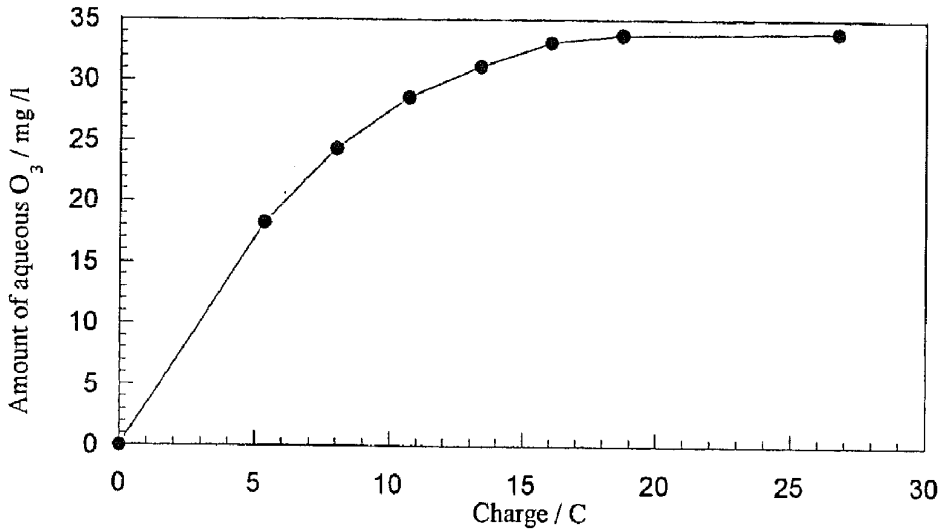
Time: 11:54:18

Fig. 1


Amount of aqueous O_3 / mg /l
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30
25
20
15
10
5
0
0
5
10
15
20
25
30
Charge / C

Fig. 2

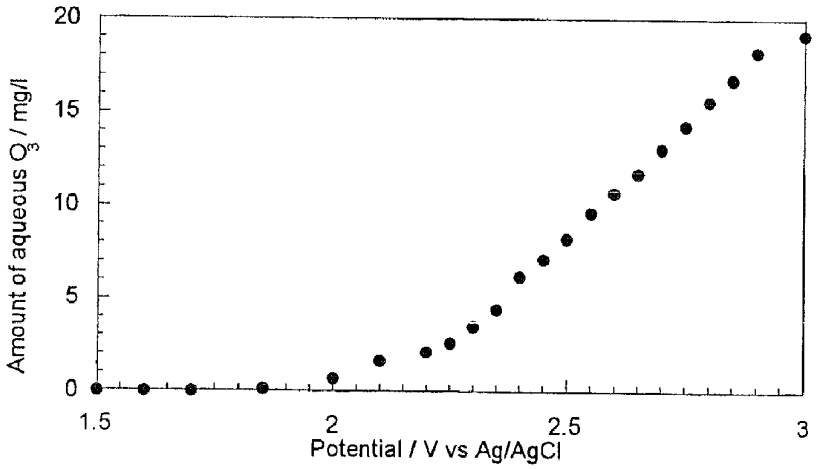
Amount of aqueous O_3 / mg/l
20
15
10
5
0
1.5
2
2.5
3
Potential / V vs Ag/AgCl

Fig. 3

DEVICE FOR AND METHOD OF GENERATING OZONE

RELATED PATENT APPLICATION

[0001] This patent application claims the benefit of U.S. Provisional Application No. 60/447,948 filed Nov. 10, 2003.

FIELD OF THE INVENTION

[0002] The present invention relates generally to the generation of ozone. In particular, the present invention relates to an electrode material for generating ozone and a method of making the electrode material. The present invention also relates to a high concentration of dissolved ozone and an ozone generation system for generating the same.

BACKGROUND OF THE INVENTION

[0003] Ozone has many industrial applications, such as destructing organic and inorganic contaminants in wastewater and sludge, households disinfectants, swimming pools and hospitals, bleaching paper, etching semiconductor surfaces, decolorizing water, removing odor from clothing, and terminating pests. [See, Bruno Langlais, David A. Reckhow, Deborah R. Brink; Ozone in Water Treatment application and Engineering, Lewis Publishers, INC. 1991, and references discussed therein.] Chlorination is commonly used in similar applications but will leave undesirable chlorinated organic residues. Ozone on the other hand will self disappear in time and leaves fewer potentially harmful residues.

[0004] There are two main types of technologies to produce ozone. The first type of technology involves the corona discharge process, wherein ozone is formed from oxygen in air by the corona discharge in an intense and high frequency alternating electric field [see, U.S. Pat. Nos. 5,882,609; 5,939,030; 6,022,456; 6,153,151]. This type of technology gives low ozone concentration (about 2% to oxygen) and can produce harmful nitrogen oxides. The generation of ozone is in the gas phase and to obtain dissolved ozone, the gaseous ozone is brought into contact with water and the amount of dissolved ozone is limited by the gas phase ozone concentration and the solubility.

[0005] The other type of ozone generation technology is an electrochemical and electrolytic process, wherein water is decomposed to ozone by passing an electric current through the electrodes immersed in an aqueous electrolyte. Since ozone is generated directly in water, this process can provide high concentration of ozone at a high current efficiency. Over 35% current efficiency has been reported at low temperatures of −30° C. to −65° C. [see, P. C. Foller, C. W. Tobias, J. Electrochem. Soc., 129 (1982), 506]. A recent report discussed a 3.0 mg/l concentration of dissolved ozone [see, Tatapudi and Fenton, J. Electrochem. Soc., 140 (1993) 3527].

[0006] In aqueous solution, ozone is formed by electrolytic decomposition of water, represented by following equations:

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^-,\ E^\circ = 1.51\ V, \quad (1)$$ and

$$H_2O + O_2 \rightarrow O_3 + 2H^+ + 2e^-,\ E^\circ = 2.07\ V. \quad (2)$$

The oxygen evolution reaction, a competitive process at a lower potential should occur more easily according to the following equation:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-,\ E^\circ = 1.23\ V. \quad (3)$$

[0007] Typically, mostly oxygen and very little ozone is generated upon electrolysis. Some devices aim for co-generation of oxygen and ozone by electrolysis of water [see U.S. Pat. No. 5,993,618]. Platinum, alpha and beta-PbO_2, Pd, Au, RuO_2-DSA's, and glassy carbon in different electrolytes have been considered and tested for ozone generation. Gold, RuO_2-DSA's, and glassy carbon have been found to have very low current efficiency (less than 1%). Platinum shows a current efficiency from 6.5% to 35% at very low temperature of about −50° C. However the current efficiency falls to around 0.5% at room temperature. Obtaining a high current efficiency at a low temperature will require additional equipment and energy cost to make existing systems less efficient and convenient. PbO_2 electrodes can produce ozone at a current efficiency of 13% at room temperature [see, U.S. Pat. No. 5,407,550]. With potassium fluoride electrolyte, a 16% current efficiency at 30° C. has been reported [see, Ten-Chin Wen and Chia-Chin Chang, J. Electrochemical Society, 140, (1993) 2764]. However, such a process releases toxic Pb ions into electrolyte solution.

[0008] U.S. Pat. Nos. 5,972,196; 5,989,407; 6,287,431 B1; 6,365,026 B1; and 6,576,096 B1 disclose dissolved ozone generators using integrated electrochemical cells. Electrodes that improve dissolved ozone concentration and current efficiency at room temperature are needed in commercial applications.

[0009] Tin dioxide, a non-toxic semiconductor, has been studied for applications in sensors, batteries and oxygen evolution. Low current efficiency and instability had been reported when such tin dioxide was used for electrochemically generating ozone in concentrated sulfuric acid.

SUMMARY OF THE INVENTION

[0010] The present invention can provide an electrode member. The electrode member can comprise a substrate member and a coating member. The substrate member can be made of a material selected from the group consisting of titanium, gold coated titanium and other inert conducting materials. The coating member can comprise a tin dioxide modified by antimony. The particles of Sn and Sb can be in an atomic ratio from about 6:1 to about 10:1. Additionally or alternatively, a predetermined amount of nickel can be added in the coating member. The coating member can comprise particles from about 3 nm to about 5 nm in size.

[0011] The electrode member of the present invention can be used for direct generation of ozone in water or through water into a gaseous state. The water can contain an electrolyte selected from the group consisting of $HClO_4$, H_2SO_4 and H_3PO_4. The electrolyte can be present in a concentration from about 0.01 M to about 0.5 M.

[0012] The present invention can also provide an ozone generation system comprising such an electrode member to generate ozone efficiently. The ozone generation system can comprise a solid polymer electrolyte, such as Nafion. Alternative, ozone can be generated in pure water, without the need of dissolved ions. The present invention can further provide a dissolved ozone with a high concentration.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The detailed description of the present invention will be better understood in conjunction with the accompanying drawings as follows:

[0014] FIG. **1** is a SEM surface morphology of an antimony doped SnO_2 electrode member of the present invention;

[0015] FIG. **2** is a graph illustrating the aqueous ozone concentration as a function of electric charge; and

[0016] FIG. **3** is a graph illustrating the instantaneous aqueous ozone concentration as a function of scan potential.

DETAILED DESCRIPTION OF THE INVENTION

[0017] Exemplary electrode members and ozone generation systems embodying the principles of the present invention will now be described in detail.

[0018] The present invention can provide an electrode member. The electrode member can comprise a substrate member and a coating member. In one exemplary embodiment, the substrate member can be made of a material selected from the group consisting of titanium, gold coated titanium and other inert conducting materials. For example, the substrate member is made of titanium. In an exemplary embodiment, the substrate member can be made of titanium and be spot-welded with a titanium wire. It will be appreciated that other materials of the substrate member are also within the scope of the present invention.

[0019] The coating member can be made of various materials and in various forms. In one exemplary embodiment, the coating member can comprise a tin dioxide. In an exemplary embodiment, the coating member can comprise an antimony modified tin dioxide film. For example, the coating member can comprise $SnCl_4\square 5H_2O$ and $SbCl_3$. In another exemplary embodiment, the coating member can comprise a predetermined amount of nickel. In one exemplary embodiment, the coating member can be in the form of a solution, before being affixed onto the substrate member. It will be appreciated that other materials and forms of the coating member are also within the scope of the present invention.

[0020] In another exemplary embodiment, the coating member can comprise particles of various sizes. For example, the coating member can comprise connected particles of less than 5 nm in size. In one exemplary embodiment, the connected particles can be from about 3 nm to about 5 nm in size. It will be appreciated that other sizes of the particles are also within the scope of the present invention.

[0021] In a further exemplary embodiment, the coating member can comprise particles of various ratios. In an exemplary embodiment, the particles of oxides of Sn and Sb can have an atomic ratio of more than 6:1. In another exemplary embodiment, the particles of oxides of Sn and Sb particles can have an atomic ratio of less than 10:1. In a further exemplary embodiment, the particles of Sb and Ni can be in an atomic ratio of more than 4:1. In a still further exemplary embodiment, the particles of Sb and Ni can be in an atomic raitio of less than 10:1. It will be appreciated that other ratios of the particles are also within the scope of the present invention.

[0022] In a preferred embodiment, the electrode member can be made of titanium and coated with antimony doped tin dioxide with surface morphology composed of 3 to 5 nm particles connected and covering substantially the entire surface. In another preferred embodiment, the particles comprise Sn and Sb in a ratio from about 6:1 to about 10:1. In a further preferred embodiment, the atomic ratio of Sn:Sb:Ni can be about 500:8:1. The electrode member can yield high concentration of dissolved ozone at room temperature with high current efficiency.

[0023] The electrode member can be prepared in various manners. In one exemplary embodiment, a substrate member and a coating member of various forms can be provided, which can be similar to those described above. If desired, the substrate member can be treated or otherwise prepared by various conventional methods. For example, the substrate member can be etch cleaned in an acid solution and then rinsed and dried. It will be appreciated that other methods of treating or preparing the substrate member are also within the scope of the present invention.

[0024] The substrate member can be affixed with the coating member in various manners. For example, the substrate member can be sprayed with, dipped into, or otherwise coated with the coating member. In an exemplary embodiment, the coating member can be sprayed with solution of 2.5 g $SnCl_4\square 5H_2O$ and 0.025 g $SbCl_3$ in 25 ml of ethanol-HCl mixture. In an exemplary embodiment, the coating member can be dipped into 25 ml ethanol-HCl mixture solution of 2.75 g $SnCl_4\square 5H_2O$ and 0.025 g $SbCl_3$. It will be appreciated that other methods of affixing the coating member to the substrate member are also within the scope of the present invention.

[0025] The coated substrate member can then be heat treated in various manners. In one exemplary embodiment, the coated substrate member can be dried, such as at a temperature of about 100° C. for about ten minutes. In another exemplary embodiment, the coated substrate member can be calcined, such as at a temperature of about 520° C. in air for 5 mins. The above coating, drying, and calcining steps can be repeated. In an exemplary embodiment, these steps can be repeat for 12 times. In another exemplary embodiment, these steps can be repeat for 20 times. It will be appreciated that other heating methods including heating temperatures and/or time periods are also within the scope of the present invention.

[0026] The present invention can also provide a high concentration ozone material. In one exemplary embodiment, approximately 35 mg/l aqueous ozone can be provided with over 15% current efficiency. In an exemplary embodiment, the 15% current efficiency only accounts for the dissolved ozone. In a preferred embodiment, such an aqueous ozone can be generated in a 6 min constant potential polarization at low electrolyte concentration at room temperate. In another exemplary embodiment, a significant amount of gaseous ozone can be generated and distinctly detected by the normal smell test. The measurement of gaseous ozone can show a much high current efficiency. The solution with dissolved ozone can decolorize a dye such as indigo instantly. High overpotential of oxygen evolution was observed in cyclic voltammetry.

[0027] Various systems can be used to generate a high concentration ozone material. In one exemplary embodiment of the present invention, an ozone generation system can be in the form of an electrochemical system for generating the high concentration ozone material. In an exemplary embodiment, the electrochemical system can comprise a cell member for containing an electrolyte material of various forms. For example, the electrolyte material can comprise $SnCl_4\square 5H_2O$ and $SbCl_3$ in an ethanol-HCl mixture. In another exemplary embodiment, ozone can be generated in pure water, without the need of dissolved ions. It will be appreciated that various other types of ozone generation systems are also within the scope of the present invention.

[0028] In one exemplary embodiment, the ozone generation system can adopt the electrode member of the present invention for generating the high concentration ozone. In an exemplary embodiment, the electrode member can be used as a working electrode. For example, the electrode member can

be used as an anode member in a electrochemical system. In another exemplary embodiment, the electrode member can be positioned on the bottom of the cell member. In a further exemplary embodiment, a constant potential can be applied to the electrode member, such as at room temperature. The constant potential can range from 1.5V to 3V with respect to a reference electrode. In an exemplary embodiment, the constant potential can be about 2.5V. It will be appreciated that various other forms of the ozone generation system are also within the scope of the present invention.

[0029] The present invention will now be describe in further detail in connection with the various Examples below.

EXAMPLE 1

[0030] A 0.8×0.8×0.05 cm^3 titanium (Ti) sheet member spot-welded with a 1 mm dia. titanium wire was first etch cleaned in a 10% boiled oxalic acid solution for 1 hour, then rinsed with distilled water and dried. An antimony doped SnO_2 electrode member was prepared by a spray pyrolysis technique on the pretreated Ti substrate member. The spray solution was 2.5 g $SnCl_4 \square 5H_2O$ and 0.025 g $SbCl_3$ in 25 ml of ethanol-HCl mixture. After drying the sprayed substrate member at 100° C. for 10 min, the substrate member was calcined at 520° C. in air for about 5 min. This treatment was repeated 12 times. The resulting electrode member showed a compact smooth surface morphology with connected particles having a diameter of about 3 to 5 nm (see FIG. **1**). The atomic ratio of Sn to Sb in the film is about 7:1 by ICP analysis.

[0031] Ozone was generated in a cell with 3 ml 0.1 M $HClO_4$. The prepared doped SnO_2 electrode member was used as a working electrode member positioned on the bottom of the cell. A 0.8 cm^2 platinum sheet was used as a counter electrode member positioned at the up-region of the electrolyte. An Ag/AgCl member was used as a reference electrode member and positioned closer to the working electrode member. A constant potential (vs. the Ag/AgCl member) of 2.5V was applied to the working electrode member at room temperature. About 35 g/l of ozone dissolved in the electrolyte was generated in about 6 min. (see FIG. **2**). The ozone concentration was determined by UV absorption as well as a standard indigo method.

EXAMPLE 2

[0032] An antimony doped SnO_2 electrode was prepared by dipping a Ti substrate with the same area as described in Example 1 into 25 ml ethanol-HCl mixture solution of 2.75 g $SnCl_4 \square 5H_2O$ and 0.025 g $SbCl_3$. Before drying the dipped the Ti substrate at 100° C., excess solution on the substrate surface was removed to leave a thin uniform liquid layer on the substrate surface. The substrate member was calcined at about 520° C. The time periods for drying and calcining were the same as in Example 1. The above process was repeated 30 times. The surface morphology of the resulting electrode was similar to that shown in FIG. **1**. The ratio of Sn to Sb in the film is about 10:1 by ICP analysis.

[0033] Ozone was generated using the same system as in Example 1. SnO_2 electrode was performed by cyclic voltammetry in a potential ranging from 1.5 V to 3 V (vs. the Ag/AgCl member) at the scan rate of 1 mV/s at room temperature. FIG. **3** shows the ozone generated against scan potential.

EXAMPLE 3

[0034] A solution of 1 molar $SnCl_4 \square 5H_2O$, 0.016 molar $SbCl_3$, and 0.002 molar $NiCl_2 \square 6H2O$ in absolute ethanol was used as the coating solution. A titanium sheet can be coated in the same manner by dip coating and pyrolysis, as described in Example 1. The coating and pyrolysis was repeated 7 times. The resulting Ni—Sb doped SnO_2 coated electrode member was tested to give better ozone generation. The current efficiency can reached more than 25% at room temperature using 0.1 molar perchloric acid electrolyte and with applied electric potential of 2.2 V (vs. the Ag/AgCl member). The ozone generation and measurement was the same as described in Example 1.

[0035] It will be appreciated that the various features described herein may be used singly or in any combination thereof. Therefore, the present invention is not limited to only the embodiments specifically described herein. While the foregoing description and drawings represent a preferred embodiment of the present invention, it will be understood that various additions, modifications, and substitutions may be made therein without departing from the spirit of the present invention. In particular, it will be clear to those skilled in the art that the present invention may be embodied in other specific forms, structures, arrangements, proportions, and with other elements, materials, and components, without departing from the spirit or essential characteristics thereof. One skilled in the art will appreciate that the invention may be used with many modifications of structure, arrangement, proportions, materials, and components and otherwise, used in the practice of the invention, which are particularly adapted to specific environments and operative requirements without departing from the principles of the present invention. The presently disclosed embodiments are therefore to be considered in all respects as illustrative and not restrictive.

What is claimed is:

1. A method of generating ozone using an electrochemical ozone generation system, the ozone generation system including an electrode member having a substrate member and an antimony modified tin dioxide coating member that further comprises nickel, the method comprising:

providing the electrode member for use as a working electrode;

applying a constant potential to the electrode member; and

generating ozone from an electrolyte.

2. The method of claim **1**, wherein providing the electrode member comprises:

providing a substrate member comprising an inert conductive material;

affixing a coating member comprising antimony modified tin dioxide and further comprising nickel to the substrate member to produce the electrode member;

drying the electrode member;

calcining the electrode member; and

repeating the drying and calcining steps a predetermined number of times.

3. The method of claim **2** wherein the coating member comprises $SnCl_4$-$5H_2O$, $SbCl_3$, $NiCl_2$-$6H_2O$ in absolute ethanol.

4. The method of claim **2**, wherein affixing a coating member to the substrate member comprises spraying a solution of $SnCl_4$-$5H_2O$ $SbCl_3$ and a nickel compound in an ethanol-HCl mixture onto the substrate member to produce a surface morphology of approximately 3 to 5 nm connected particles covering substantially all of the substrate member.

5. The method of claim **2**, wherein affixing a coating member to the substrate member comprises dipping the substrate member into a solution of $SnCl_4$-$5H_2O$ $SbCl_3$ and a nickel compound in an ethanol-HCl mixture to produce a surface morphology of approximately 3 to 5 nm connected particles covering substantially all of the substrate member.

6. The method of claim **2**, wherein drying the electrode member comprises heating the electrode member at about 100° C. for about 10 minutes.

7. The method of claim **2**, wherein calcining the electrode member comprises calcining the electrode member at a temperature of about 520° C. in air for about 5 minutes.

8. The method of claim **2**, wherein repeating the drying and calcining steps a predetermined number of times comprises repeating the drying and calcining steps between 12 and 30 times.

9. The method of claim **1**, wherein applying a constant potential to the electrode member comprises applying between approximate 1.5V to 3V of constant potential at room temperature to the electrode member.

10. The method of claim **1**, wherein generating ozone from an electrolyte comprises generating approximately 35 mg/l aqueous ozone.

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